



Vanadia supported on zeolites for SCR of NO by ammonia

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ABSTRACT

Vanadia supported on zeolites were prepared and characterized by N_2 physisorption, FTIR, XRPD, and $\text{NH}_3\text{-TPD}$ methods. The influence of the Si/Al ratio on the total surface acidity of the catalysts as well as the optimum V_2O_5 content were studied and compared with the catalytic activity in the selective catalytic reduction (SCR) of NO with ammonia. The SCR activity was found to correlate directly with the total acidity of the catalysts and showed high poisoning resistivity after doping with potassium oxide ($100 \mu\text{mol/g}$). The poisoning resistance was due to unique combination of high surface area, acidity and micropore structure of the support. Apparently the support hosted the potassium oxide on the acid sites, thereby protecting the active vanadium species from poisoning. Zeolite based catalysts might therefore prove useful for SCR of NO in alkali-containing flue gases from, e.g. biomass fired power plants.

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1. Introduction

Generally, nitrogen oxides are generated from stationary sources such as, e.g. industrial boilers, gas turbines, steam power plants, waste incinerators, marine engines, and petrochemical plants. The selective catalytic reduction (SCR) is considered an useful approach for removing nitrogen oxides generated from stationary sources in views of economic and technological efficiency [1–4]. A wide number of catalysts have been reported for the effective removal of nitric oxide by ammonia as the reducing agent. All the catalysts can broadly be classified into three types namely noble metals, metal oxides and zeolites. Noble metals are very active for the reduction of NO, but not selective to N_2 because of ammonia oxidation. Accordingly, noble metal catalysts have been replaced by metal oxide catalysts for conventional SCR and zeolites for high temperature SCR applications because of their thermal stability. The industrial metal oxide catalysts for the commercial SCR process are based on TiO_2 -supported $\text{V}_2\text{O}_5\text{-WO}_3$ and $\text{V}_2\text{O}_5\text{-MoO}_3$ oxides. The use of TiO_2 as a support is limited by the fact that it exists in more crystalline phases and possesses low resistance to sintering, low surface area and high costs. Most industrial SCR systems use vanadium-based catalysts which restricts the operating temperature range to 300–420 °C in order to obtain sufficient NO_x conversion efficiency.

At higher temperatures (above 420 °C) the oxidation of ammonia competes with the SCR reaction on vanadium-based catalysts

ultimately forming nitrogen oxides [5]. The loss of selectivity via ammonia oxidation is severe, actually so much that commercial use is limited to temperatures below 420 °C. Moreover, the temperature constraint limits the flexibility of the location of the SCR catalyst in the flue gas duct and adds additional costs for heat exchangers where the exhaust temperature exceeds this temperature limitation. These disadvantages are potentially overcome by using zeolites as support materials [6,7].

While SCR is a well-proven technology, its application with non-conventional fuels like biomass brings specific challenges. In particular, deactivation of the catalyst by biomass-containing alkali metals and subsequent activity reduction is problematic. Several authors [8–12] have reported the deactivation effect of alkaline metals on the activity of $\text{V}_2\text{O}_5/\text{TiO}_2$ catalysts. Most of them conclude that poisonous additives (e.g. potassium, barium) are affecting the Brønsted acid sites, which are responsible for the ammonia adsorption, thus decreasing both their number and activity in NO reduction. The relative decrease in catalytic activity after doping with potassium is well correlated with decrease in total acidity of the catalysts [8–12]. Most of these studies are done on TiO_2 and sulphated ZrO_2 supports with relatively low surface area and thermal stability.

Strategic approaches to overcome the alkali metal deactivation include use of highly acidic support materials and a high vanadium content to maintain a high number of active sites, thus making the catalyst less susceptible for deactivation by alkali metals. Vanadium-containing zeolites have already found considerable interest due to their catalytic properties (acidity and high surface area) in a variety of reactions including the SCR reaction [7,13–15].

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Acidity and surface area of the zeolites are easily tunable with maximum values observed with compositions corresponding to Si/Al ratios of 10–25 [16,17]. Acidity is needed to host the poisonous alkali metals, whereas high surface area is needed to achieve high V₂O₅ content without forming crystalline phases with high capability of ammonia oxidation.

Pence and Thomas [18] first documented HMORDENITE catalysts as being active for the selectively reduction of NO_x to N₂ using NH₃ as a reducing agent and thus created interest in the use of zeolites as SCR catalysts. Concurrently, Seiyama et al. [19] investigated the SCR activity of various transition metal ion-exchanged Y zeolite catalysts. Promising results obtained here led to a variety of later studies focusing on the enhancement in SCR activity by exchanging metals (e.g., Fe, Cu, Ni, Pt, Rh, Co, Ga, etc.) into different zeolites (e.g., Y, MORDENITE, ZSM5, FERRIERITE, BETA). Among metal exchanged zeolites Fe and Cu are well known and quite active for the SCR of NO with NH₃ [20–22]. Based upon these studies, it is evident that proper selection of the metal can greatly enhance the activity of SCR catalysts. It is interesting to note, however, that the SCR activity and selectivity of these same metals is low if the metals are not exchanged into appropriate zeolites.

In the present work, the Si/Al ratio of the zeolite support and the V₂O₅ content were optimized for various zeolites to achieve maximum activity in the SCR reaction. The influence of potassium oxide additives on the activity was also studied and compared with traditional SCR catalysts. All the catalysts were characterized by various techniques to allow detailed discussion of the effect of the catalyst composition on the SCR performance.

2. Experimental

2.1. Catalyst preparation and characterization

Commercial NH₄-ZSM5, NH₄-BETA, NH₄-MORDENITE and NH₄-Y zeolites (Zeolyst International, USA) with different Si/Al were initially calcined at 550 °C for 5 h to obtain the HZSM5 (400 m²/g), HBETA (680 m²/g), HMORDENITE (500 m²/g) and HY (700 m²/g) supports, respectively. V₂O₅-zeolite catalysts with 3–16 wt.% V₂O₅ were prepared by wet impregnation of the supports with 0.5–1.25 M vanadium oxalate solution. This vanadium oxalate solution was prepared from ammonium metavanadate and oxalic acid in the molar ratio 1:2 at 70 °C. After catalytic activity measurements the most active catalysts were poisoned by incipient wet impregnation with a 0.05 M solution of KNO₃ (Aldrich, 99.999%) to obtain a potassium loading of 100 μmol/g. Each impregnated catalyst was oven dried at 120 °C for 12 h followed by calcination at 500 °C for 4 h prior to use.

X-ray powder diffraction (XRPD) measurements were performed on a Philips PW 1820/3711 powder diffractometer using Ni-filtered Cu K_α radiation within a 2θ range of 10–60° in steps of 0.02°. FTIR spectra of the samples were recorded on a Perkin-Elmer 1710 spectrometer at ambient conditions in KBr disks (1 mg in 100 mg). BET surface area and micropore volume of the samples were determined from nitrogen physisorption measurements on about 100 mg sample at liquid nitrogen temperature (77 K) with a Micromeritics ASAP 2010 instrument. The samples were heated to 200 °C for 1 h prior to measurements.

NH₃-TPD experiments were conducted on a Micromeritics Autochem-II instrument. In a typical TPD experiment, about 100 mg of dried sample was placed in a quartz tube and pretreated in flowing He at 500 °C for 2 h. Then, the temperature was lowered to 100 °C and the sample was treated with anhydrous NH₃ gas (Air Liquide, 5% NH₃ in He). After NH₃ adsorption, the sample was flushed with He (50 ml/min) for 100 min at 100 °C. Finally, the TPD operation was carried out by heating the sample from 100 to 650 °C (10 °C/min) under a flow of He (25 ml/min).

2.2. Catalytic activity measurements

The SCR activity measurements were carried out at atmospheric pressure in a fixed-bed quartz reactor loaded with 50 mg of fractionized (180–300 μm) catalyst samples positioned between two layers of inert quartz wool. The reactant gas composition was adjusted to 1000 ppm NO, 1100 ppm NH₃, 3.5% O₂ and balance He for dry conditions and additional 2.3% H₂O for wet conditions (gas passed through a humidifier at room temperature) by mixing 1% NO/He ($\pm 0.1\%$ abs.), 1% NH₃/He (0.005% abs.), O₂ ($\geq 99.95\%$) and balance He ($\geq 99.999\%$) (Air Liquide) using Bronkhorst EL-Flow F-201C/D mass-flow controllers. The total flow rate was maintained at 300 ml/min (ambient conditions). During the experiments the temperature was raised stepwise from 200 to 540 °C while the NO and NH₃ concentrations were continuously monitored by a Thermo Electron Model 10A chemiluminiscent NO-NO_x gas analyzer. At each set-temperature the N₂O concentration was further measured by gas chromatography (Shimadzu-14B GC, TCD detection, Poraplot column) after ensuring steady state conditions by maintaining the temperature for at least 30 min.

The catalytic activity is represented as the first-order rate constant k(cm³/(g s)), since the SCR reaction is known to be first-order with respect to NO under stoichiometric NH₃ conditions [23,24]. The first-order rate constants were obtained from the conversion of NO as:

$$k = -(F_{\text{NO}}/(m_{\text{cat}} C_{\text{NO}})) \ln(1 - X)$$

where F_{NO} denotes the molar feed rate of NO (mol/s), m_{cat} the catalyst mass, C_{NO} the NO concentration (mol/cm³) in the inlet gas and X the fractional conversion of NO.

3. Results and discussion

The results of the N₂-BET surface area and micropore volume measurements are summarized in Table 1 for V₂O₅/HZSM5 catalysts with various Si/Al ratios. Increased Si/Al ratio from 15 to 140 of the V₂O₅/HZSM5 catalysts resulted in an increase of the total surface area from 370 to 410 m²/g, whereas the micropore volume values remained unchanged and similar as found for other zeolites [25,26].

Fig. 1 shows the FTIR spectra of the pure and V₂O₅ impregnated HZSM5 catalysts in the range of 1300–400 cm⁻¹. All the catalysts exhibited typical skeletal vibrations of MFI zeolite structure. The bands at 1225 and 1102 cm⁻¹ are due to external and internal asymmetric stretching vibrations and that of 800 and 630 cm⁻¹ are due to symmetric stretching vibrations in the MFI lattice. The bands at 550 cm⁻¹ are assigned to the vibrations of the double five rings in the MFI lattice [27]. The absorption band near 450 cm⁻¹ is due to the vibrations of the SiO₄ and AlO₄ internal tetrahedra [25]. The ratio of intensities of the bands at 550 and 450 cm⁻¹ is indicative of the zeolite crystallinity [25]. In the impregnated samples only a shoulder band at 980 cm⁻¹ assigned to monomeric V=O anchored to the aluminosilicate surface was observed (magnified view). This is generally considered to be a proof of the incorporation of highly dispersed vanadium into the framework, and the band can easily be distinguished from those present in the pure HZSM5 (15) reference sample. Nakagawa et al. [28] have reported the V=O bond stretching frequency at 980 cm⁻¹ in the IR spectra of vanadium oxide monolayer species supported on titania.

Temperature-programmed desorption (TPD) of ammonia or pyridine is a frequently used method for determining the surface acidity of solid catalysts as well as acid strength distribution. Ammonia is often applied as a probe molecule because of its small molecular size, thermal stability and high basic strength (pK_a=9.2) [29]. In the present investigation, the acidity measurements have been carried out by the NH₃-TPD method. Fig. 2 shows NH₃-TPD

Table 1

Surface area, pore volume and NH₃-TPD characterization results of 3%V₂O₅/HZSM5 catalysts.

Catalyst	Surface area (m ² /g)	Micropore volume (cm ³ /g)	Acidity (μmol/m ²)	T _{max} 1 (°C)	T _{max} 2 (°C)
3%V ₂ O ₅ /HZSM5 (15)	370	0.11	3.00	216	421
3%V ₂ O ₅ /HZSM5 (25)	374	0.11	2.17	198	414
3%V ₂ O ₅ /HZSM5 (40)	386	0.11	1.70	180	400
3%V ₂ O ₅ /HZSM5 (140)	410	0.11	0.11	176	365

Catalyst names with the numbers (15), (25), (40) and (140) represents Si/Al ratio of the support.

T_{max}1 (°C) and T_{max}2 (°C) are low temperature (100–300 °C) and high temperature (300–500 °C) NH₃-TPD regions, respectively.

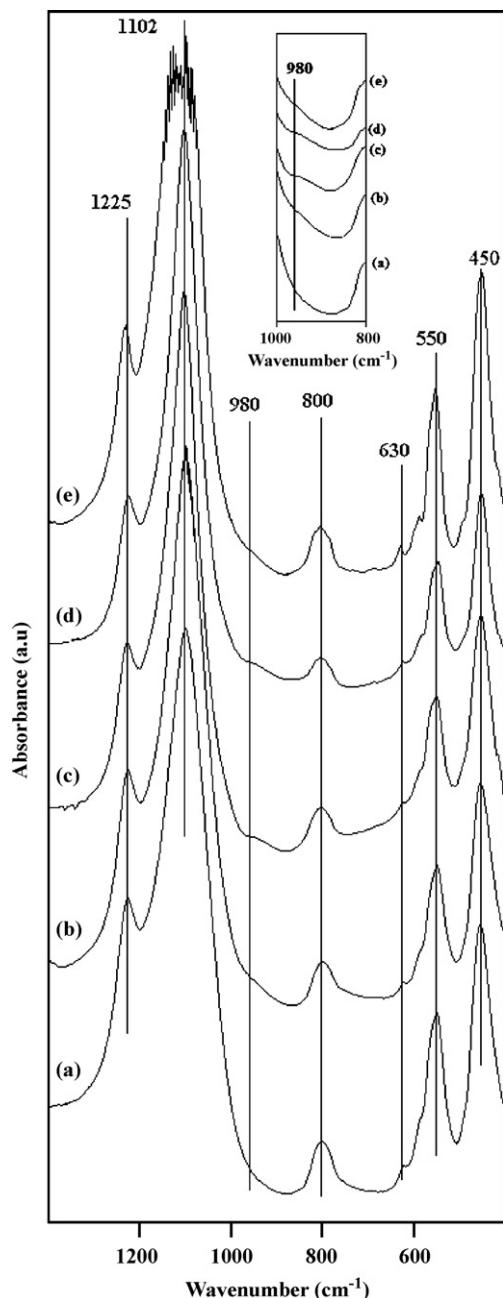


Fig. 1. FTIR spectra of 3% V₂O₅/HZSM5 catalysts with different Si/Al ratios. (a) HZSM5 (15), (b) V₂O₅/HZSM5 (15), (c) V₂O₅/HZSM5 (25), (d) V₂O₅/HZSM5 (40), (e) V₂O₅/HZSM5 (140).

profiles of 3%V₂O₅/HZSM5 catalysts in the temperature range of 100–650 °C. The results of the NH₃-TPD measurements are summarized in Table 1. Generally, the catalysts showed two ammonia desorption regions; one due to moderate acid strength (high T_{max}2

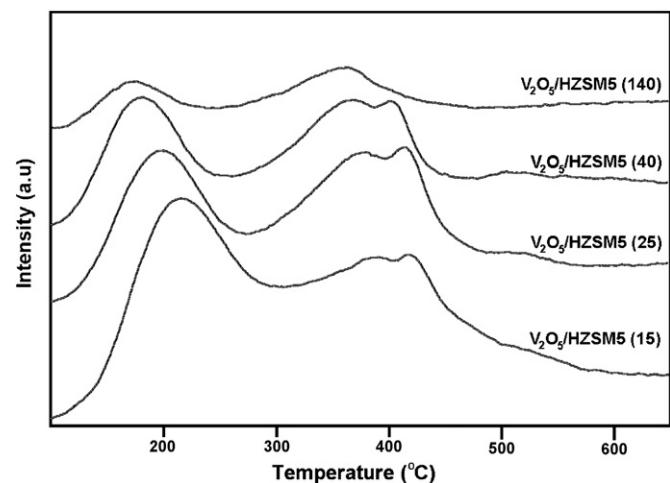


Fig. 2. NH₃-TPD profiles of 3% V₂O₅/HZSM5 catalysts with different Si/Al ratios.

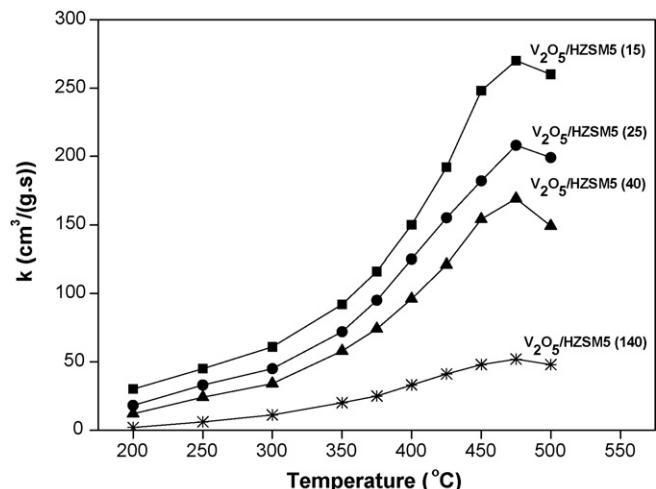


Fig. 3. Catalytic activity profiles of 3% V₂O₅/HZSM5 catalysts with different Si/Al ratios under dry conditions.

region) and the other due to weak acid strength (low T_{max}1 region). The T_{max}1 peak attributed to the weak acid sites was observed at around 200 °C, while the T_{max}2 peak attributed to the strong acid sites was observed around 400 °C. The V₂O₅/HZSM5 (15) catalyst with the highest content of aluminum revealed very large T_{max}1 and T_{max}2 peaks, indicating its high acid site density. The proportion of weak acid sites was further reduced compared to that of strong acid sites. An increase in the Si/Al ratio of the V₂O₅/HZSM5 catalysts resulted in a significant decrease in intensity of both the T_{max}1 and T_{max}2 peaks. The temperature at the maximum of the desorption peaks was also shifted slightly towards a lower temperature with increasing Si/Al ratio of the catalysts. This gradual temperature shift may be due to a decrease in the acid site density,

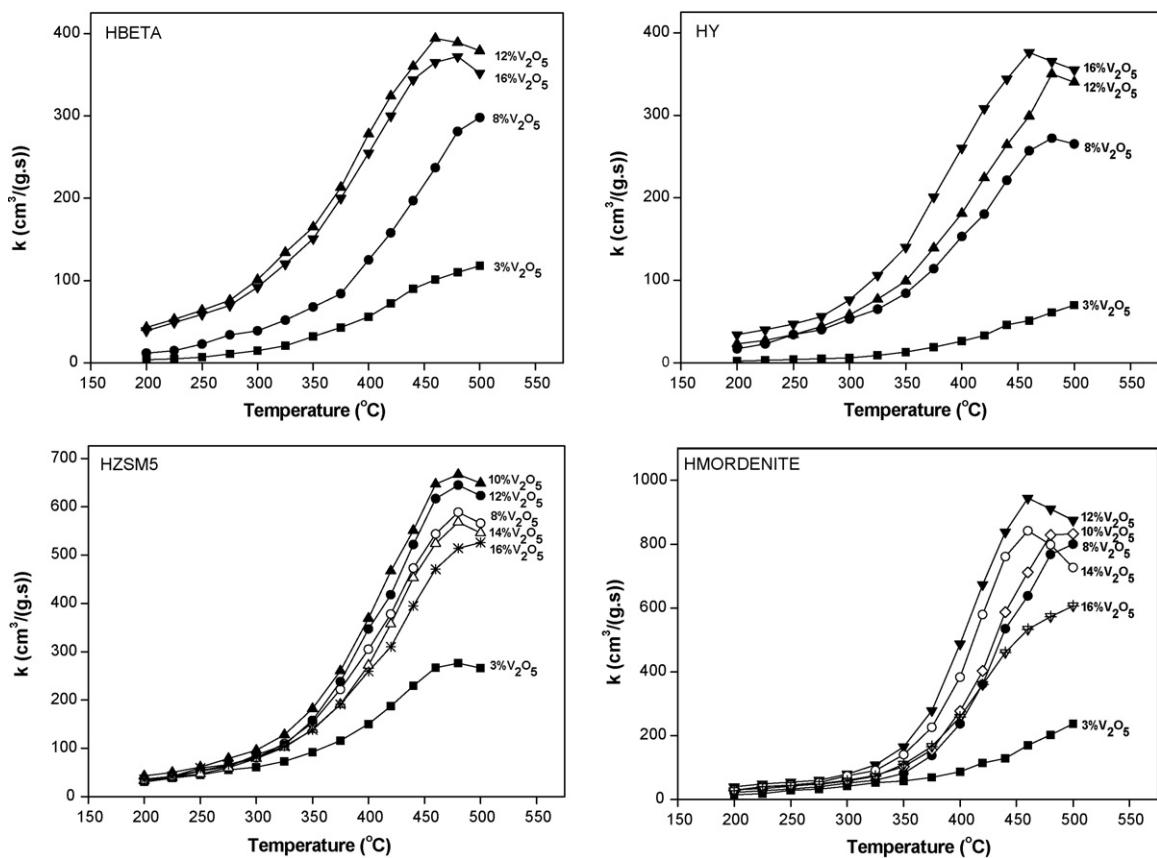


Fig. 4. Catalytic activity profiles of various zeolites with different V_2O_5 content under dry conditions.

which hamper the readsorption of ammonia on the acid sites in the pores during its desorption [30,31].

Fig. 3 shows the catalytic activity profiles of V_2O_5 /HZSM5 catalysts with different Si/Al ratios measured under dry conditions. Change in activity was observed for all the catalysts in the examined temperature range of 200–500 °C. Maximum rate constant was observed at 475 °C and decreased thereafter with temperature due to the increased rate for ammonia oxidation. With increase in Si/Al ratio of the support a decrease in rate constant was observed (270 vs 40 $\text{cm}^3/(\text{g.s})$ when increasing Si/Al ratio from 15 to 140) thus clearly demonstrating the relation between activity and the catalyst acidity. It is well known that the NO activity and the acidity of zeolite supports are connected, as also observed by Andersson et al. [32] in their study on SCR of NO over acid-leached MORDENITE catalysts. With increasing Si/Al ratio there will be a decrease in acidity of catalysts as observed in the TPD studies (vide supra). Additionally, the catalyst activity might also be affected by the nature and concentration of active vanadium species at exchange sites. With these observations other zeolite materials like HBETA, HY and HMORDENITE were selected with lower Si/Al ratios of 25, 12 and 10, respectively. The observed rate constant values were less compared to that of reported catalysts [8,9]. This might be due to less surface content of V_2O_5 on this high surface area support materials. Thus the V_2O_5 content was increased up to 16 wt%.

Fig. 4 shows the catalytic activity profiles obtained on various alternative zeolites with different V_2O_5 content under dry conditions. With increasing V_2O_5 content the rate constant was increased up to a certain loading and thereafter decreased. This trend has also been seen in V_2O_5/TiO_2 systems due to formation of polymeric species that are more active than the monomeric species [12,33]. Hence, a higher reactivity of polymeric metavanadate species compared to isolated vanadyls, as well as a faster reduction by NH_3 and

a faster reoxidation by gaseous oxygen of the polymeric metavanadate groups was also reported. However, when overloaded with V_2O_5 , aggregated vanadium species with high activity for ammonia oxidation appeared to lead to decreased overall SCR activity.

In all the alternative zeolite catalysts, no diffraction peak corresponding to crystalline V_2O_5 was observed (Fig. 5) and only pure support patterns were reflected in the XRD. The most intense crystalline V_2O_5 phases are expected at $2\Theta = 20.3^\circ$, 26.1° and 30.9° . Moreover, all catalysts were highly dispersed and well below the V_2O_5 monolayer surface coverage. To achieve

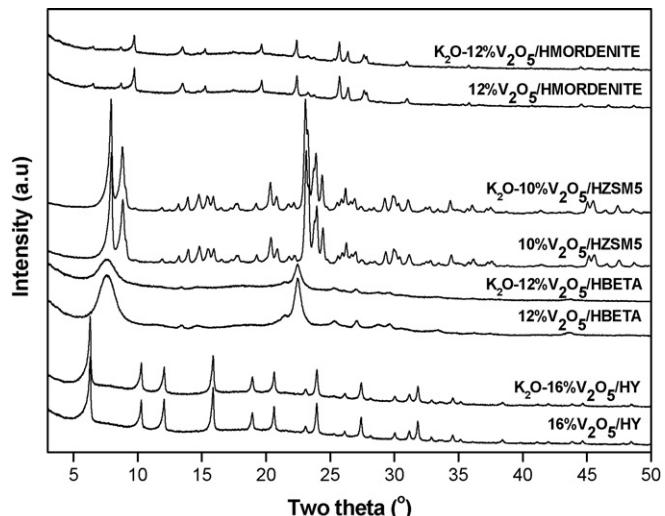


Fig. 5. XRD patterns of undoped and potassium-doped catalysts with optimum V_2O_5 content.

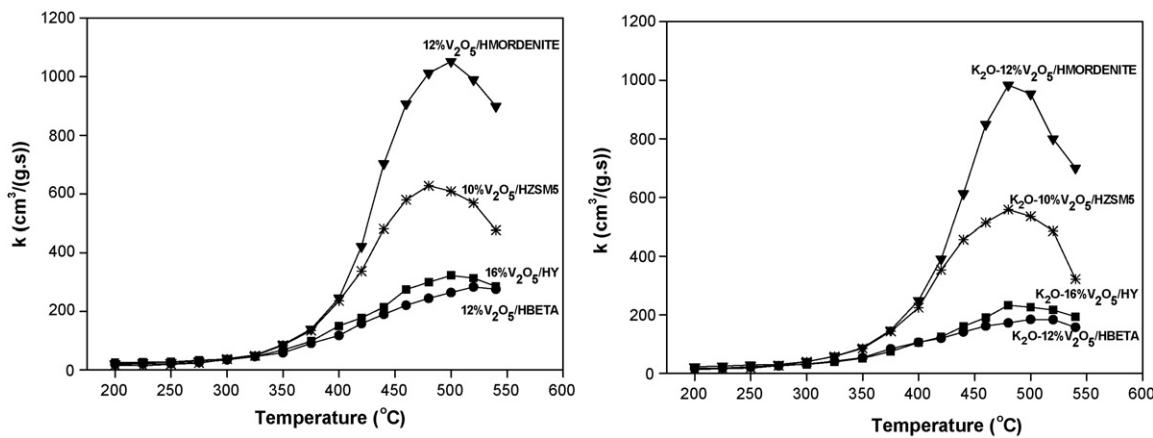


Fig. 6. Catalytic activity profiles of undoped and potassium-doped catalysts with optimum V_2O_5 content under wet conditions.

monolayer capacity a surface density of $8 \text{ VO}_x/\text{nm}^2$ is needed [34]. Among all the examined supports 12% V_2O_5 /HMORDENITE showed highest rate constant followed by 10% V_2O_5 /HZSM5, 12% V_2O_5 /HBETA and 16% V_2O_5 /HY. 12% V_2O_5 /HMORDENITE catalysts showed a maximum rate constant value of $944 \text{ cm}^3/(\text{g.s})$ whereas 10% V_2O_5 /HZSM5, 12% V_2O_5 /HBETA and 16% V_2O_5 /HY catalysts showed maximum rate constant values of 667, 394 and $376 \text{ cm}^3/(\text{g.s})$, respectively. All the optimum catalysts showed maximum rate constant at 460°C except the 10% V_2O_5 /HZSM5 catalyst, which showed maximum rate constant at 480°C .

From the data compiled in Table 2, a relationship between the catalytic activity and the various types of optimized zeolite catalysts including the textural and the acidity characteristics of the zeolite catalysts can be found. The most obvious parameter to be considered, namely the type of zeolite support, which determines the size of the micropores, seems very relevant since HZSM5 and HMORDENITE catalysts with 0.10 and $0.13 \text{ cm}^3/\text{g}$ micropore volumes featured a higher activity than the HY and HBETA catalysts with corresponding micropore volumes of 0.24 and $0.19 \text{ cm}^3/\text{g}$, respectively. Bartholomew et al. [35,36] also found that MORDENITE and ZSM5 catalysts were superior to Y-zeolite for the SCR process due to enhanced formation of the 3H structure (i.e., NH_4^+ bonded through three hydrogen bonds with $\text{Al}(\text{OH})_3\text{H}^-$) by small pore zeolites. This structural characteristic is apparently associated with the formation of an especially SCR active ammonia complex, which explain the high activity of HMORDENITE and HZSM5 as compared with HBETA and HY zeolites.

The results of the NH_3 -TPD are also summarized in Table 2. The order of the acidity and the SCR activity of the catalysts was: 12% V_2O_5 /HMORDENITE > 10% V_2O_5 /HZSM5 > 12% V_2O_5 /HBETA >

16% V_2O_5 /HY. All the catalysts showed $T_{\max 1}$ peak at around 175 – 190°C , while the strong acid sites $T_{\max 2}$ peak was significantly increased to 410°C for the HMORDENITE catalyst due to its high acid site density. It was also interesting to see the influence of vanadium presence on support in enhancing the total acid sites. Pure zeolites exhibited acid site density ($\mu\text{mol}/\text{m}^2$) values of 2.83 , 2.53 , 2.15 and 2.07 for HMORDENITE, HZSM5, HBETA and HY, respectively. When the supports were impregnated with vanadium enhanced acid site density ($\mu\text{mol}/\text{m}^2$) values of 4.58 , 3.72 , 3.24 and 2.42 for 12% V_2O_5 /HMORDENITE, 10% V_2O_5 /HZSM5, 12% V_2O_5 /HBETA and 16% V_2O_5 /HY, respectively. Hence, both structural and acidic characteristics favored the HMORDENITE catalysts in SCR of NO compared to the other catalysts, in accordance with the activity measured.

It is very important to study the influence of water on the performance of SCR catalysts since water most often is present in the flue gas. Most authors, with few exceptions [37], agree that water hamper the SCR reaction [38–40] and has a mechanistic influence on the SCR activity as proposed by Topsøe et al. [39,40]. Fig. 6 shows the catalytic activity profiles obtained under wet conditions for the optimum zeolite catalysts. Among all the supports HMORDENITE showed the highest rate constant followed by HZSM5, HY and HBETA. Importantly, the rate constant value of 12% V_2O_5 /HMORDENITE ($430 \text{ cm}^3/(\text{g.s})$) catalyst was comparable to that of commercial V_2O_5 – WO_3 – TiO_2 catalyst ($500 \text{ cm}^3/(\text{g.s})$) reported in the literature [9] at 420°C reaction temperature. Moreover, maximum catalytic activity was shifted towards higher temperatures in the presence of water, thus clearly indicating an inhibition effect of water on the SCR reaction at low temperatures. This inhibition effect is probably a result of water adsorption on

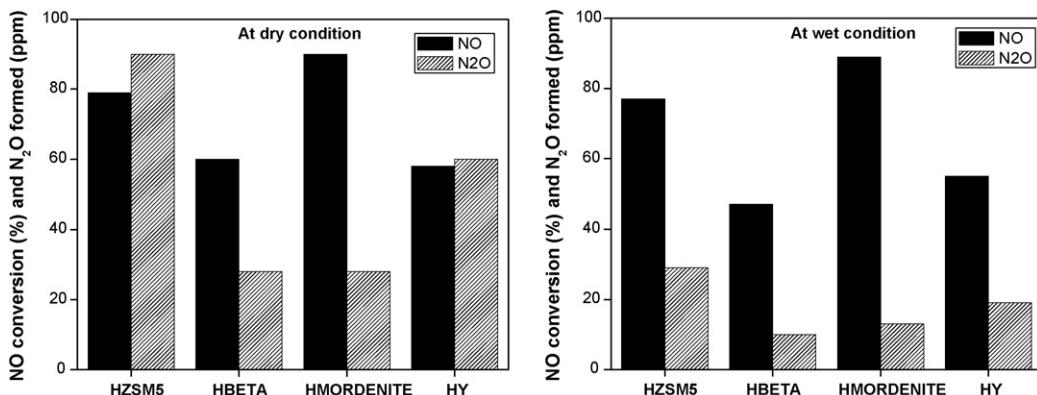


Fig. 7. NO conversion and N_2O formation for zeolite catalysts with optimum V_2O_5 content on zeolites at 500°C under dry and wet conditions.

Table 2

Maximum rate constant, surface area, pore volume and NH₃-TPD characterization results of undoped and potassium-doped catalysts with optimum V₂O₅ content.

Catalyst	<i>k</i> _{max} (cm ³ /(g s))	Surface area (m ² /g)	Micropore volume (cm ³ /g)	Acidity (μmol/m ²)	<i>T</i> _{max1} (°C)	<i>T</i> _{max2} (°C)
16%V ₂ O ₅ /HY	323	524	0.24	2.42	176	321
12%V ₂ O ₅ /HBETA	284	510	0.19	3.24	184	339
10%V ₂ O ₅ /HZSM5	628	324	0.10	3.72	188	376
12%V ₂ O ₅ /HMORDENITE	1052	348	0.13	4.58	188	410
K ₂ O-16%V ₂ O ₅ /HY	233	488	0.23	2.00	171	318
K ₂ O-12%V ₂ O ₅ /HBETA	185	497	0.18	3.04	179	330
K ₂ O-10%V ₂ O ₅ /HZSM5	558	298	0.09	3.59	184	370
K ₂ O-12%V ₂ O ₅ /HMORDENITE	983	322	0.12	4.56	177	396

*T*_{max1} (°C) and *T*_{max2} (°C) are low temperature (100–300 °C) and high temperature (300–500 °C) NH₃-TPD regions, respectively.

the catalyst surface at lower temperature. By increasing the reaction temperature, water can be expected to desorb from the pores of zeolites and thus circumvent the inhibition effect. On the other hand, the positive role of water being present was seen in terms of a drastic decrease in N₂O formation at 500 °C (Fig. 7). The HMORDENITE catalyst showed high conversion and selectivity as compared to the other catalysts. Especially, HZSM5 and HY catalysts were forming relatively high amounts of N₂O. This clearly shows that the ammonia oxidation reaction, responsible for the N₂O formation, was suppressed under wet conditions even at elevated temperatures. Catalytic activity of zeolite supports was studied in wet conditions at 420 °C. Supports showed rate constant (cm³/(g s)) values of 46, 38, 28 and 26 for HMORDENITE, HZSM5, HBETA and HY, respectively. All these rate constant values are well below 10% of the NO conversion.

The results of the N₂-BET surface area, surface density of V₂O₅, micropore volume and acidity measurements are also summarized in Table 2 for potassium-doped catalysts. Upon the addition of potassium the surface area and pore volume slightly decreased, which can be the result of specific interaction of the potassium with the support material as well as partial physical blocking of the support pores. Total acidity of the potassium oxide doped catalysts also decreased slightly compared to the analogous undoped samples. Furthermore, the *T*_{max1} and *T*_{max2} positions of the potassium doped catalyst shifted about 10 °C to lower temperatures, indicative of lower relative strengths of the acid sites. Assuming that potassium oxide first occupy the strongest acid sites present on the support and then weakens the remaining acid sites due to electron donation, the *T*_{max} should be expected to shift towards lower temperature region, as observed.

Doping the optimum catalysts with potassium (100 μmol/g) resulted in slight decrease in activity and a small shift of maximum catalytic activity towards lower temperature (Fig. 6). Especially the HMORDENITE catalyst showed increased resistance to the alkali poisoning and was deactivated by 9% only at 500 °C, whereas the other catalysts with HZSM5, HY and HBETA support material were deactivated by 11%, 30% and 35%, respectively at their *T*_{max} temperatures. The deactivation was even lower at 400 °C, the temperature of operation in most power plants. The observed change in catalytic activity after doping with potassium seemed to correlate well with the loss in total acidity of the catalysts (listed in Table 2). In general, high dispersion of vanadium, high surface area and high surface acidity of zeolites enable hosting of potassium oxide with relatively little change in total acidity. Consequently, the potassium deactivation was significantly lower in the present catalysts compared to that of traditional SCR catalysts. In traditional catalysts 45% deactivation has been observed at around 400 °C on highly active V₂O₅–WO_x/ZrO₂ catalyst with even less potassium loading, i.e. of 80 μmol/g [41]. The important deactivation resistance parameters for metal oxide support materials suggested by Due-Hansen et al. [9] are low vanadium coverage (below monolayer), high surface area, and high surface acidity. These three crucial parameters are all reached by the HZSM5 and HMORDENITE catalysts studied in

this work. For zeolite supports an additional structural parameter concerned with the size of micropores can also alter the SCR catalytic activity [33,34], as also found in this study.

4. Conclusions

The catalytic behavior of vanadia supported on zeolite catalysts with different Si/Al ratios was tested for the SCR of NO with ammonia. The SCR activity was found to be directly correlated to the total acidity of the catalysts. On the surface of these zeolites the V₂O₅ was highly dispersed and amorphous in nature. Impregnation with vanadium and subsequent poisoning with potassium oxide caused only small change in the micro-pore structure of the zeolites. Interestingly, potassium-doped HZSM5 and HMORDENITE catalysts showed high resistance for potassium deactivation, because of the unique nature of the material exhibiting higher surface acidity than the conventional V₂O₅–WO_x/ZrO₂ or TiO₂ catalysts. Further studies in a pilot plant with potassium chloride aerosol exposure are in progress, and a possible application of these alkali-tolerant SCR catalysts in biomass fired power plants will be evaluated.

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